STUDIES ON THE IONIZATION EQUILIBRIA OF SILICIC ACID AND POLYSILICATE EQUILIBRIA IN HIGH TEMPERATURE BRINES*

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Relatively high concentrations of silica sometimes occur in hydrothermal waters with polymerization and precipitation upon cooling. In slightly basic solutions silicic acid ionizes to form monosilicates and sometimes polysilicates. The ionization behavior and polysilicate formation are best studied by precise potentiometry using cells such as were developed at ORNL in programs supported by the Division of Physical Research of ERDA. We have nearly completed the experimental part of a detailed study of some of these equilibria using titration techniques in a hydrogen-electrode concentration cell to examine polysilicate formation in 1 m NaCl solutions at temperatures from 60° to 290°C and at Si(IV) concentrations 0.005 m to 0.05 m. At the lowest concentration only mononuclear species occur over wide temperature and pH ranges. At hydroxyl numbers from about 0.6 to 1.0 (average charge-per-silicon) small polysilicates which equilibrate rapidly occur at higher Si(IV) concentrations. A re-examination of the early work of Ingri at 25°C will be described as well as conclusions regarding the most probable formulas of the polysilicates in the basic solutions.

The most significant equilibrium reaction,

$$Si(OH)_4 + OH^- \rightleftarrows SiO(OH)_3^-,$$

is being determined (uncertainties of about 0.02 log units) from 0.1 m NaCl to 5.0 m and to about 300°C. Values of the logarithm of the equilibrium quotient for the above reaction are 3.82 and 2.22 at 60°C and 296°C in 1 m NaCl and 4.18 to 2.28 at the same two temperatures in 5 m NaCl. When measurements are completed at lower salt concentrations we will give an anlytical expression from which the thermodynamic quantities for the reaction can be derived. The reaction has also been defined in the proton dissociation form by making measurements on the dissociation of water under these same conditions.

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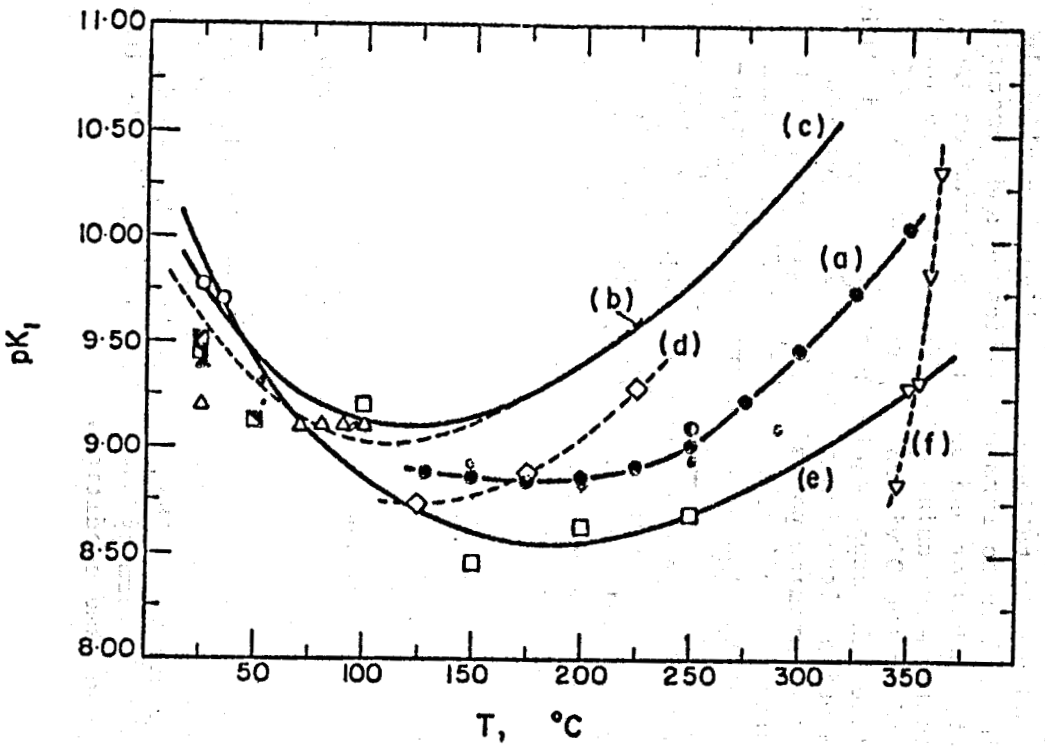
DISCLAIMER



Previous estimates of pK_1 of silicic acid at elevated temperatures and including some data available at lower temperatures; ● (curve a)—this work; (curve b)—calculated curve of COBBLE (1964); (curve c)—calculated curve of VOLOSOV *et al.* (1972); ◇ (curve d)—from CRERAR and ANDERSON's (1971) data as calculated by VOLOSOV *et al.* (1972); □ (curve e)—conductance measurements and equation by RYZHENKO (1967); ▽ (curve f)—from solubility measurements of VILIM (1961); ○—GREENBERG and PRICE (1957); ◐—Learned (1966); △—VAN LIER *et al.* (1960); ◪—LAGERSTRÖM (1959); ◩—INGRI (1959); ▲—HARMAN (1928).

Seward (1974).

ORNL DWG. 71-8168R

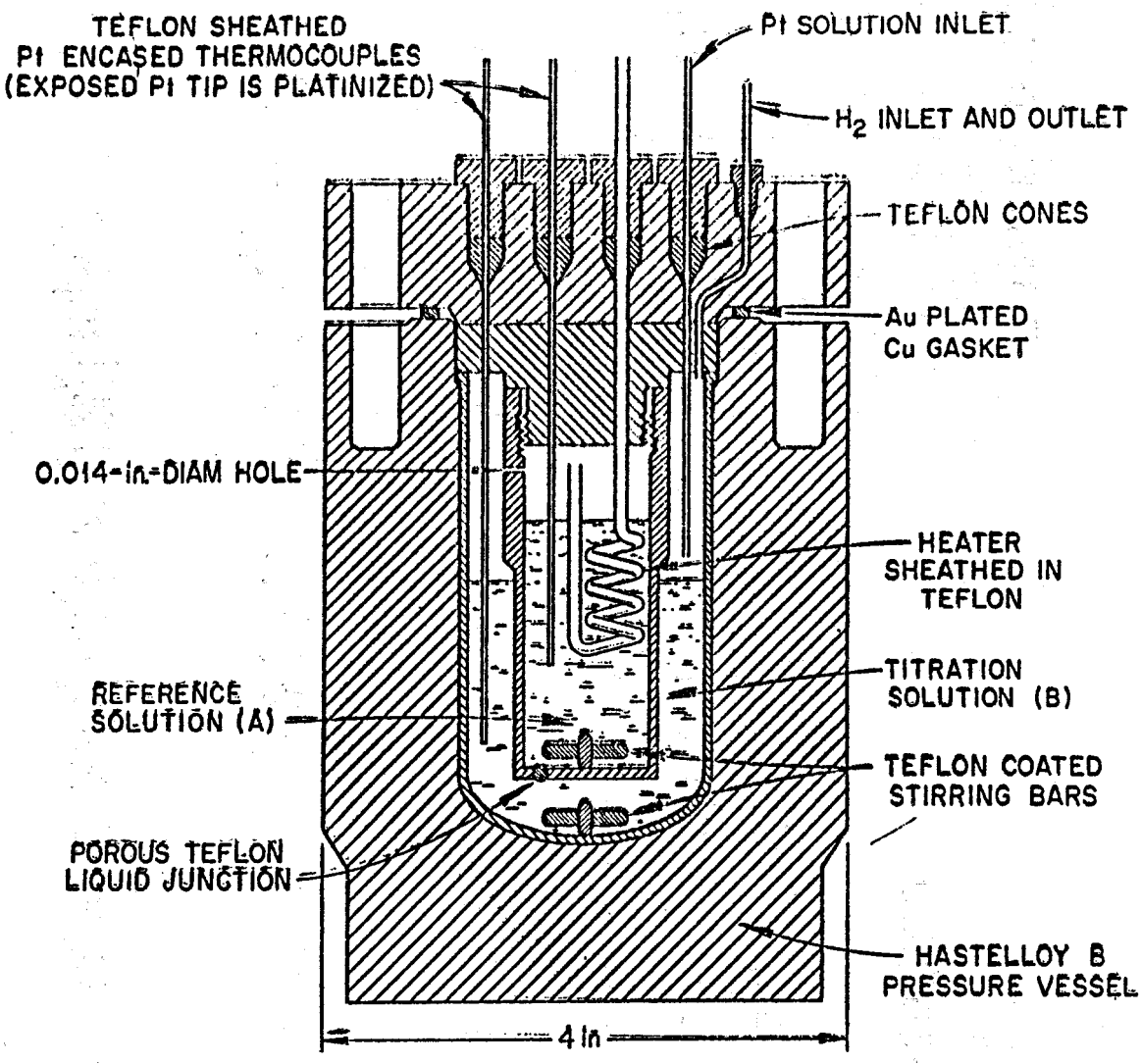
Cell Representation:

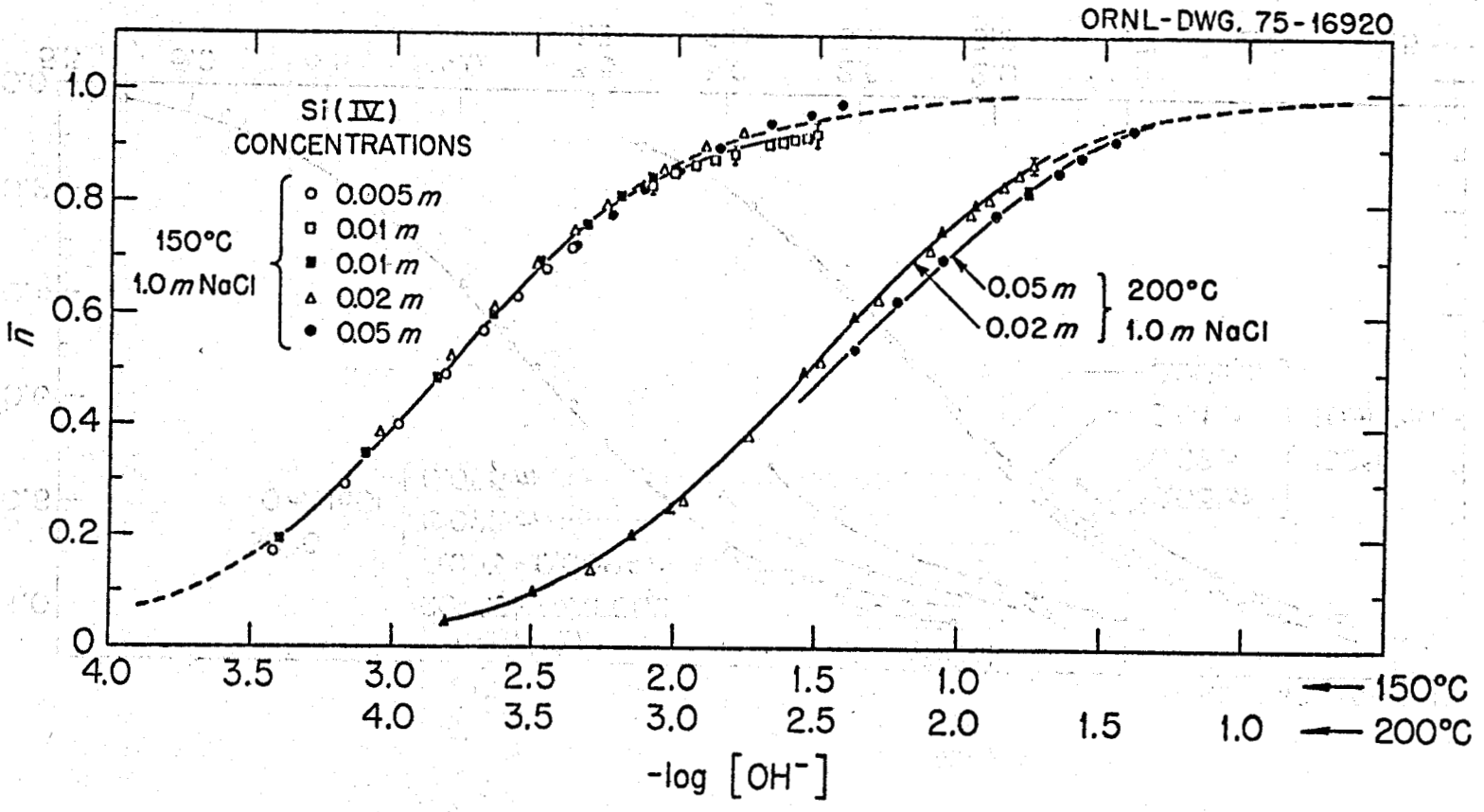
$$\text{Pt, } H_2 \;\Big|\; \begin{matrix} a\ m\ \text{NaCl} \\ b\ m\ \text{Si(OH)}_4 \\ c\ m\ \text{NaOH} \end{matrix} \;\Big\|\; \begin{matrix} a\ m\ \text{NaCl} \\ 0.02\ a\ m\ \text{NaOH} \end{matrix} \;\Big|\; \text{Pt, } H_2$$

Cell Voltage:

$$\Delta E = \frac{RT}{F} \ln \left([OH^-] / [OH^-]_r \right) - \Sigma\, D_i \left(m_{i,r} - m_i \right)$$

$$D_i = RT\lambda_i |Z_i| Z_i F \Sigma \left(|Z_i| m_i \lambda_i \right)$$


TEFLON SHEATHED
Pt ENCASED THERMOCOUPLES
(EXPOSED Pt TIP IS PLATINIZED)
Pt SOLUTION INLET
H_2 INLET AND OUTLET
TEFLON CONES
Au PLATED
Cu GASKET
0.014-in.-DIAM HOLE
HEATER
SHEATHED IN
TEFLON
TITRATION
SOLUTION (B)
REFERENCE
SOLUTION (A)
TEFLON COATED
STIRRING BARS
POROUS TEFLON
LIQUID JUNCTION
HASTELLOY B
PRESSURE VESSEL
4 in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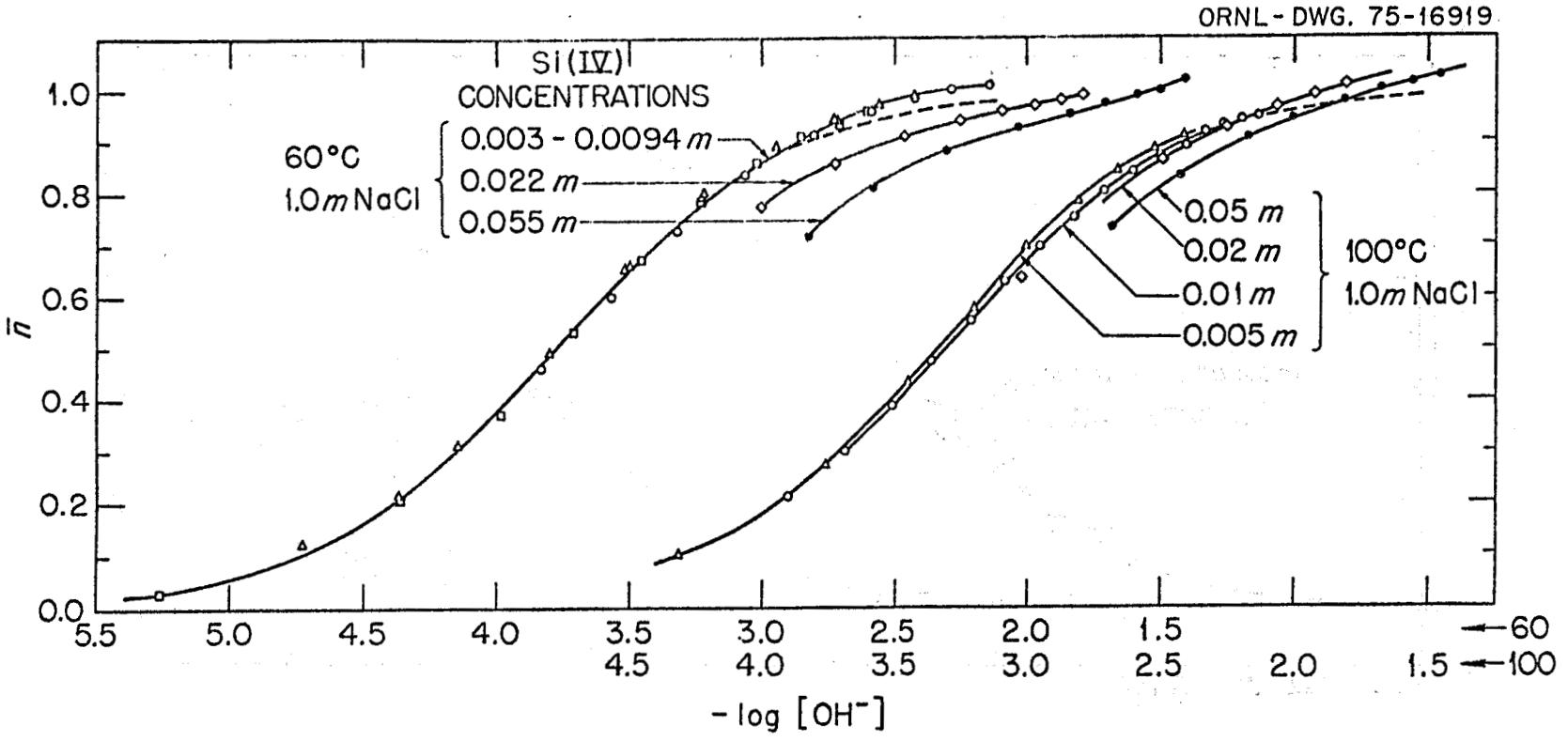
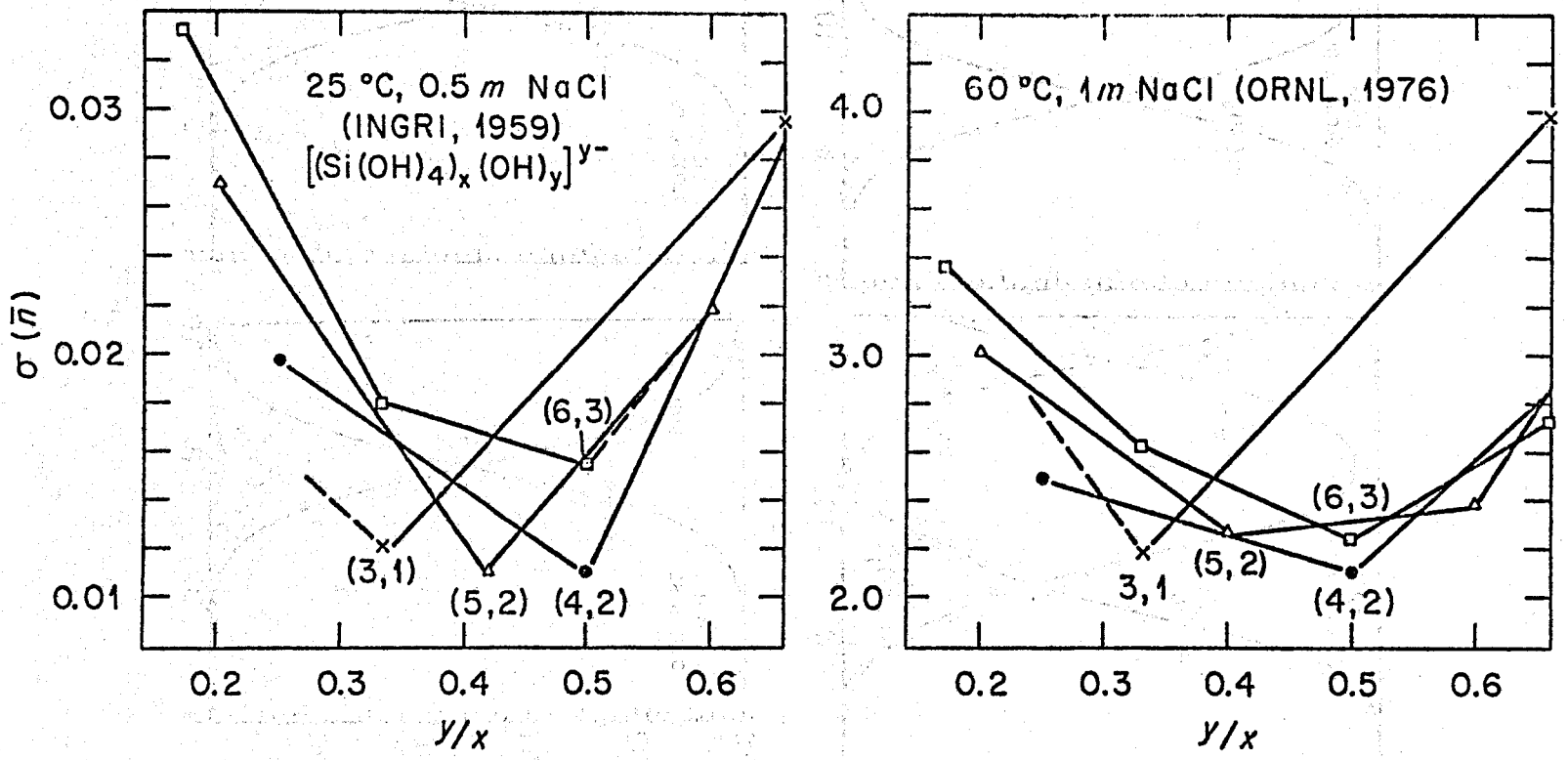
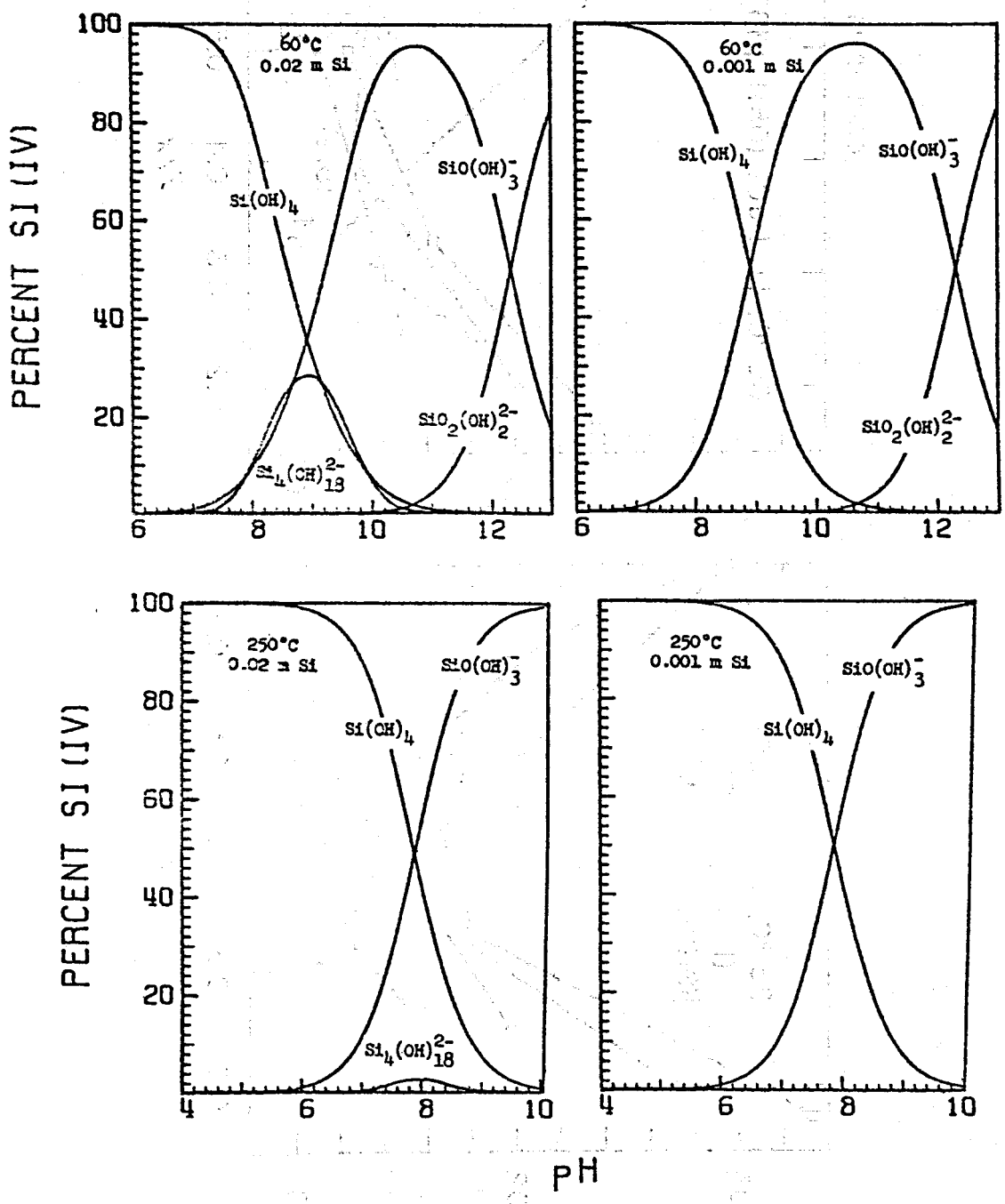
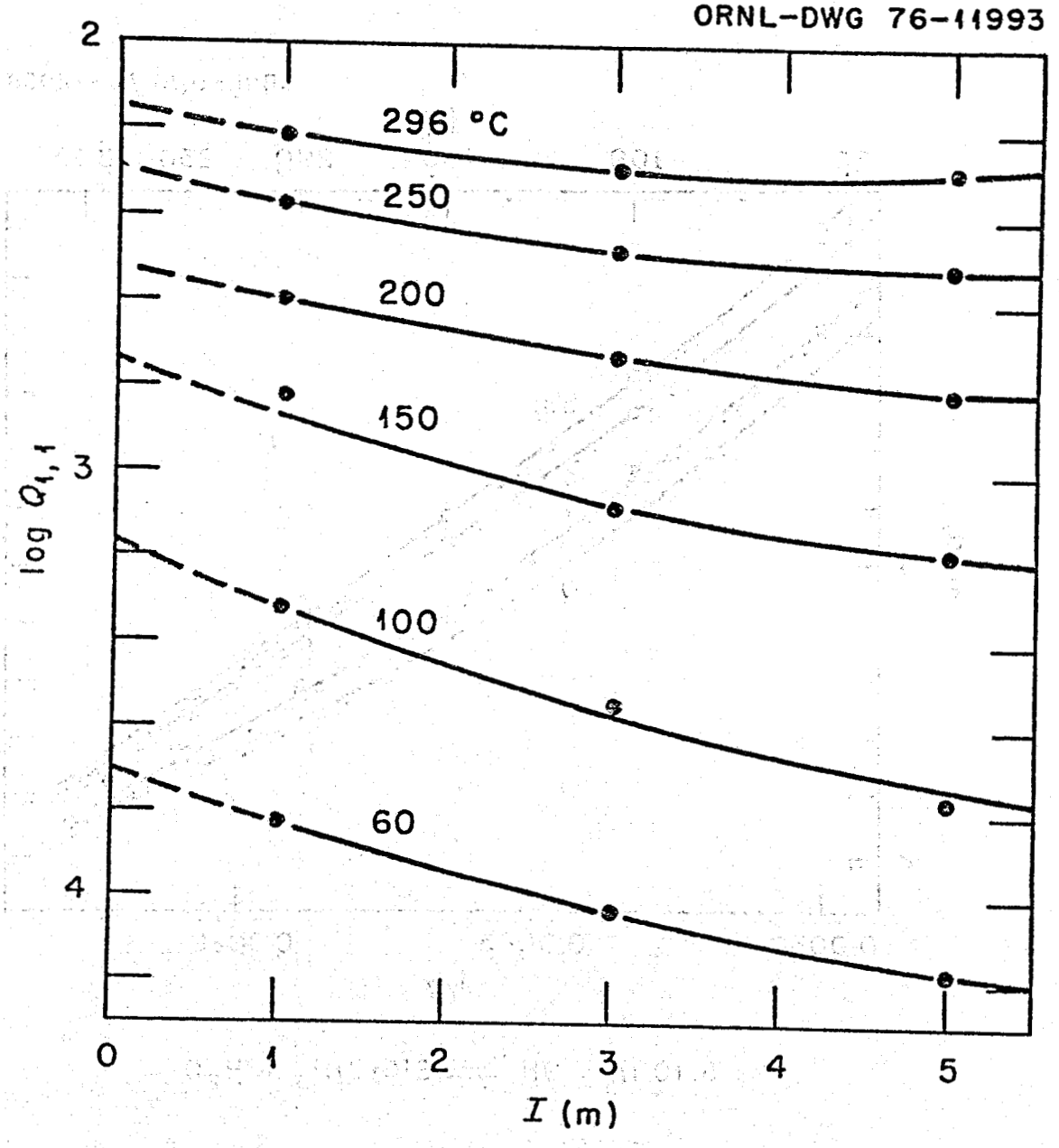
Si(IV)
CONCENTRATIONS
150°C
1.0 m NaCl
0.005 m
0.01 m
0.01 m
0.02 m
0.05 m
0.05 m
0.02 m
200°C
1.0 m NaCl
$\bar{n}$
1.0
0.8
0.6
0.4
0.2
0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
150°C
200°C
-log [OH⁻]


ORNL - DWG. 75-16919
Si(IV)
CONCENTRATIONS
60°C
1.0 m NaCl
0.003 - 0.0094 m
0.022 m
0.055 m
0.05 m
0.02 m
0.01 m
0.005 m
100°C
1.0 m NaCl
$\bar{n}$
1.0
0.8
0.6
0.4
0.2
0.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
60
100
- log [OH⁻]

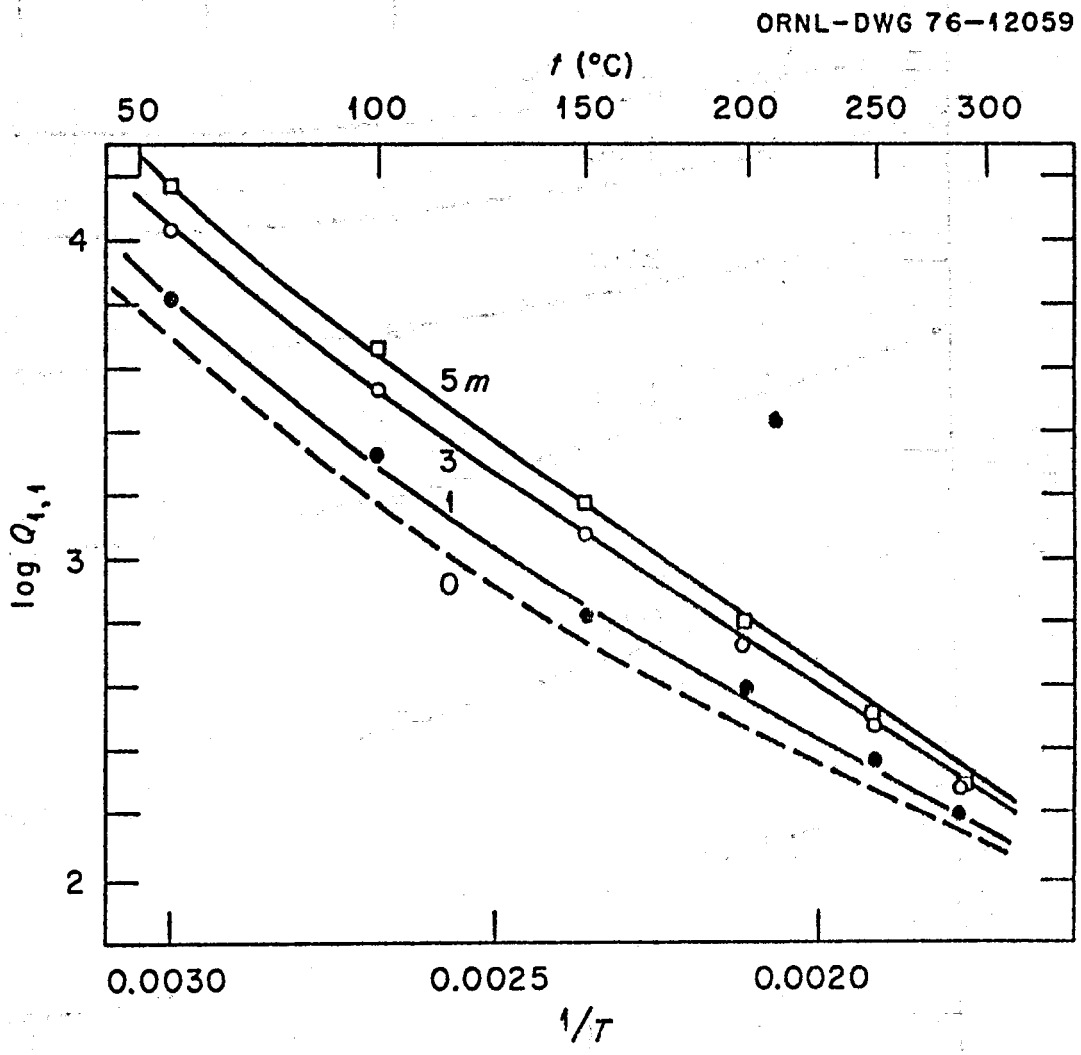
ORNL-DWG 76-11994




PERCENT SI (IV)
100
80
60
40
20
60°C
0.02 m Si
Si(OH)4
SiO(OH)3-
SiO2(OH)2 2-
Si4(OH)18 2-
6
8
10
12
60°C
0.001 m Si
Si(OH)4
SiO(OH)3-
SiO2(OH)2 2-
6
8
10
12
PERCENT SI (IV)
100
80
60
40
20
250°C
0.02 m Si
SiO(OH)3-
Si(OH)4
Si4(OH)18 2-
4
6
8
10
250°C
0.001 m Si
SiO(OH)3-
Si(OH)4
4
6
8
10
PH



$$Si(OH)_4 + OH^- \overset{Q_{1,1}}{\rightleftharpoons} SiO(OH)_3^- + H_2O$$



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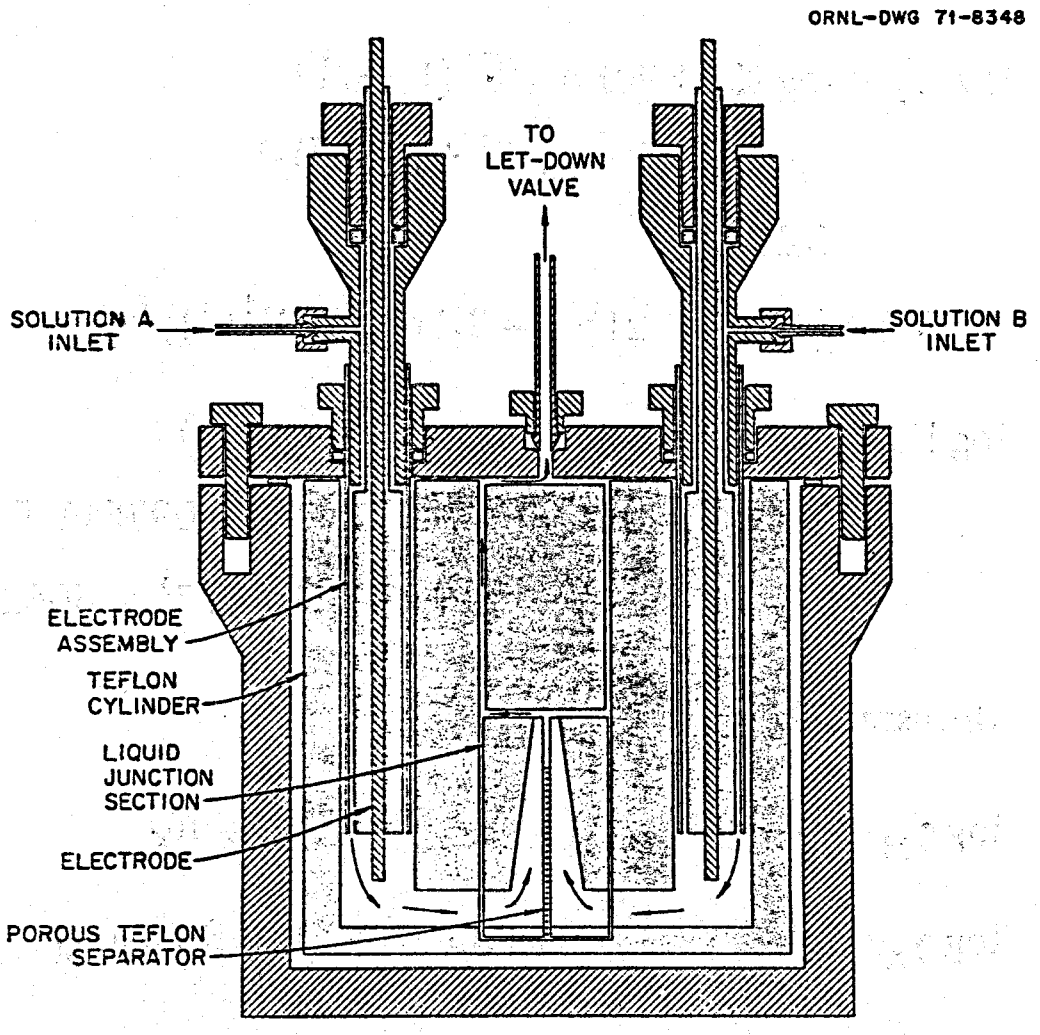


Schematic Plan of Flowing EMF Cell

Ionization H_2O in NaCl Solutions

$$\log Q'_w = \log K_w + 2.0\, A\sqrt{I}/(1+\sqrt{I}) - [p_1 + p_2/T + p_3\, T^2 + p_4\, F(I)]\, I - 0.0157\phi\, I$$

$$F(I) = [1 - (1 + 2I^{1/2} - 2I)\exp(-2I^{1/2})]/4I$$

$\log K_w$ (taken from previous determinations)

$$= 3.1286 \times 10^4 + 94.9734 \ln T - 0.097611\, T - 2.17087 \times 10^6\, T^{-2} - 606.522\,.$$

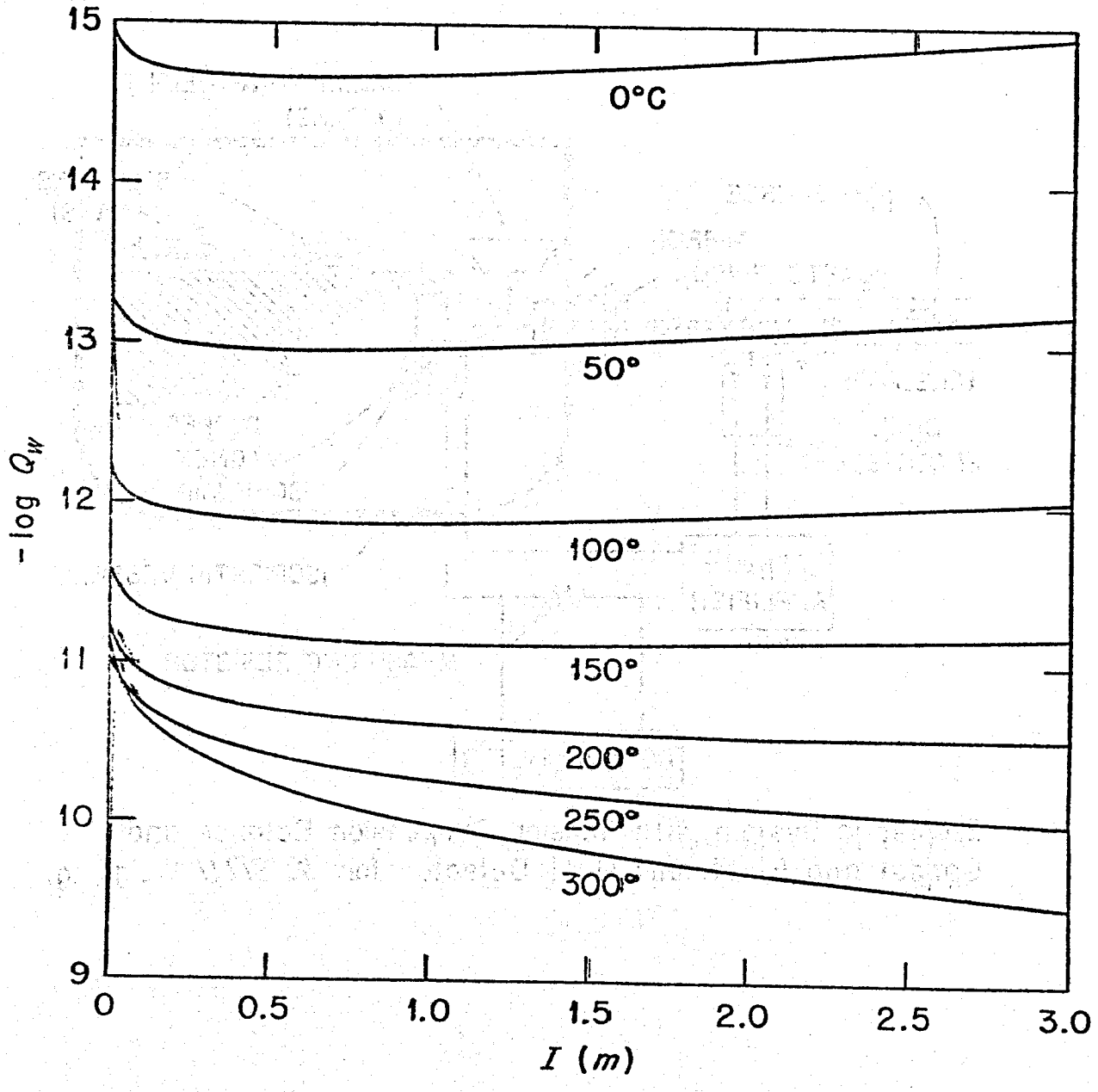
Bronsted-Guggenheim:

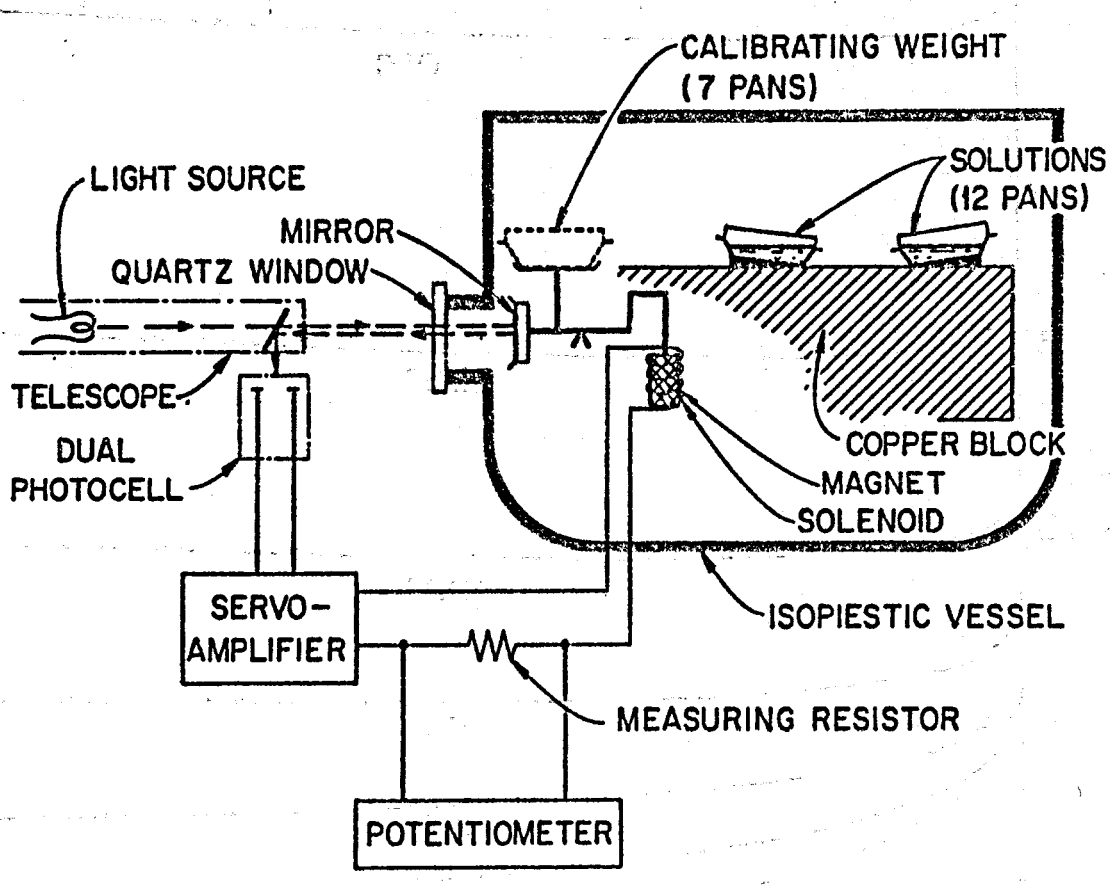
$$\log \gamma_{M'} = -Z^2_{M'}\, A\sqrt{I}/(1+\sqrt{I}) + \sum_X B_{M'X} m_X$$

$$\log \gamma_{X'} = -Z^2_{X'}\, (= Z^2_{X'})\, A\sqrt{I}/(1+\sqrt{I}) + \sum_M B_{MX'} m_M$$

From Pitzer:

$$B_{MX} = B^0_{MX} + B^1_{MX}\, F(I)$$


15
14
13
12
11
10
9
- log Q_w
0°C
50°
100°
150°
200°
250°
300°
0
0.5
1.0
1.5
2.0
2.5
3.0
I (m)



Isopiestic System with Torsion Suspension Balance and Optical and Electronic Null Detector for *IN SITU* Weighing.